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## In Situ and On-Site Bioremediation

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## ENHANCED REDUCTIVE DECHLORINATION OF TCE IN A BASALT AQUIFER

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**ABSTRACT:** A field evaluation of enhanced reductive dechlorination of trichloroethene (TCE) in ground water has been in progress since November 1998 to determine whether in situ biodegradation can be significantly enhanced through the addition of an electron donor (lactate). An in situ treatment cell was established in the residual source area of a large TCE plume in a fractured basalt aquifer utilizing continuous ground water extraction approximately 150 meters downgradient of the injection location. After a 1-month tracer test and baseline sampling period, the pulsed injection of lactate was begun. Ground water samples were collected from 11 sampling points on a biweekly basis and in situ water quality parameters were recorded every 4 hours at two locations. Within 2 weeks after the initial lactate injection, dissolved oxygen and redox potential were observed to decrease substantially at all sampling locations within 40 m of the injection well. Decreases in nitrate and sulfate concentrations were also observed. Both quantitative in situ rate estimation methods and qualitative measures such as changes in redox conditions, decreases in chlorine number, and changes in biomass indicator parameters are being used throughout the test to evaluate the extent to which biodegradation of TCE is enhanced.

### INTRODUCTION

Test Area North (TAN) at the Idaho National Engineering and Environmental Laboratory is the site of a nearly 2-mile long trichloroethene (TCE) plume resulting from the injection of liquid waste directly into the fractured basalt of the Snake River Plain Aquifer during the 1960s. While most of the plume has TCE concentrations less than 1 mg/L, a high concentration core exists in the immediate vicinity of the former injection well (where a residual source of TCE remains) with ground water concentrations ranging from 1.5 mg/L to over 300 mg/L. Co-disposed organic materials have provided an electron source to drive limited intrinsic reductive dechlorination in the vicinity of the former injection well. The complete reductive dechlorination pathway for chloroethenes is as follows:  $\text{PCE} \rightarrow \text{TCE} \rightarrow \text{DCE} \rightarrow \text{VC} \rightarrow \text{ethene}$  (Freedman and Gossett, 1989). In each step of the process the compound is reduced through substitution of a chlorine atom by a hydrogen atom.

The evidence for intrinsic reductive dechlorination at TAN is derived largely from 9 years of ground water monitoring data. These data include significant concentrations of DCE, with the *cis*-DCE isomer predominating. Low levels of vinyl chloride, ethene, and ethane have also been observed in the former injection well. Dissolved oxygen was found to be less than 1 mg/L for a distance of about 150 m downgradient. Nitrate concentrations in the immediate vicinity of the former injection well were depressed and low levels of methane have been

detected. While localized areas of strongly reducing (methanogenic) conditions seemed to exist, the bulk redox conditions in the high concentration core appeared to range from nitrate-reducing to sulfate-reducing. In addition to ground water monitoring data, the potential for complete dechlorination of TCE at TAN was demonstrated through fed-batch bioreactor studies using basalt core collected from the plume as the inoculum. Rapid TCE disappearance accompanied by ethene and ethane generation was observed in bioreactors fed lactate. Accumulation of ethene and ethane was not observed in the controls.

Based on the preliminary field and laboratory data, a field evaluation of enhanced reductive dechlorination was initiated in the fall of 1998. The primary objective of the evaluation is to determine whether in situ TCE degradation can be significantly enhanced through the addition of an electron donor. It is believed that the addition of a suitable electron donor will foster the growth of the indigenous microbes, driving the aquifer to a more reducing state throughout the treatment cell. This has the potential to increase the rate and extent of reductive dechlorination where it is already occurring, and to stimulate the process over a larger area.

## **EXPERIMENTAL DESIGN AND OPERATION**

The field evaluation of enhanced reductive dechlorination of TCE at TAN entails the periodic injection of high concentrations of an electron donor solution into Well TSF-05 (the former waste injection well) with ground water monitoring throughout the treatment cell. In order to exert some control on the distribution and residence time of the electron donor in the subsurface, a hydraulic gradient was induced through pumping. The test was designed to create a 150-m long treatment cell in the high concentration core between Wells TSF-05 and TAN-29, a downgradient extraction well (Figure 1). The induced flow conditions are likely to cause a corresponding change in the distribution of contaminants and other groundwater solutes and parameters of interest independent of electron donor addition. For this reason historical groundwater sampling results cannot be used as the basis for comparison when evaluating the effect of electron donor addition.

**Start-up Period.** In order to separate the effect of the new flow conditions on contaminant distributions from the effect of electron donor addition, the pumping and injection system was operated and monitored for almost two months prior to lactate addition. This allowed a new baseline to be established for contaminant and other groundwater solutes and parameters of interest. Chloroethenes, competing electron acceptors, redox potential, temperature, pH, conductivity, and nutrients were all measured approximately weekly during the start-up period.

The start-up period was used not only to establish the baseline for relevant parameter distributions, but also to establish the baseline for flow and transport in the aquifer under the conditions of the field evaluation. This was accomplished by adding a conservative tracer (bromide) to the injection line at TSF-05 at the beginning of the start-up period. The objective was to determine the groundwater flow velocity and the aquifer dispersion by measuring tracer breakthrough at the monitoring wells in the treatment cell. The aquifer pressure response was also

measured during the start-up period to aid calibration of the numerical model to be used for data evaluation.

**Enhanced Reductive Dechlorination Evaluation.** After completion of the start-up period, electron donor addition was begun. In the laboratory studies using enrichment cultures from TAN, lactate was found to be a much better electron donor than glucose or methanol. Based on this information and on its success in other studies (e.g., DeBruin et al., 1992; Gibson and Sewell, 1992; Fennel et al., 1997), lactate was chosen as the electron donor. The design average in situ lactate concentration was 200 mg/L based on the results of the laboratory bioreactor studies. The lactate was injected into Well TSF-05 as a 60% sodium lactate solution on a weekly basis. Pulsing should aid with in situ mixing and the high concentrations should help to prevent biofouling of the injection well because they will inhibit microbial growth. The initial pulsing frequency and concentration can be modified as necessary to improve the distribution of lactate in situ.

The monitoring network for the enhanced ISB field evaluation at TAN is shown in Figure 1. Well TAN-37 is being sampled at two depths in order to take advantage of its open-hole completion. All of the wells are being sampled using dedicated, low flow, submersible pumps. With the exception of Wells TAN-10A and TAN-27 (which are sampled monthly) all of the wells are being sampled biweekly. The parameters being monitored and their significance are given in Table 1. In addition to ground water sampling, in situ sondes are being used to collect dissolved oxygen, redox potential, specific conductivity, pH, and temperature in Wells TAN-37 and TAN-31. These were included in the monitoring design in an attempt to better resolve the temporal effects of lactate injection than would be possible through ground water sampling.

**Data Analysis.** The overall objective of the enhanced ISB field evaluation is to determine whether the biodegradation of TCE through ARD can be enhanced through addition of an electron donor supply. The quantitative criterion established for demonstrating that biodegradation can be significantly enhanced at TAN is the degradation rate for must be observed to increase for two consecutive quarters of groundwater monitoring with the final rate equaling or exceeding twice the baseline rate. As data become available, the biodegradation rate will be estimated using several first-order methods including: graphical extraction, the Buscheck and Alcantar (1995) analytical approach, and the Wiedemeier et al. (1996b) tracer-corrected approach. A numerical model will also be utilized to estimate the rates through inverse modeling.

In addition to the quantitative evaluation criterion, many other qualitative parameters have been identified which will aid in the interpretation of the field evaluation results. In particular the time variations of the following parameters are expected to contribute to the overall analysis: chloroethene concentrations, electron donor concentrations, reaction product concentrations, electron acceptor concentrations, redox potential, biomass indicators, and micronutrient concentrations. Ultimately, performance of the field evaluation will also demonstrate whether the ISB system can be adequately monitored and will provide information that can be used to estimate long-term operations cost.

## PRELIMINARY RESULTS

As of January 1999, the start-up period has been completed and three weekly lactate injections have occurred. Tracer and baseline monitoring results are presented and the initial effects of lactate injection in the treatment cell are discussed.

**Tracer and Baseline Monitoring.** During the start-up period, potable water was continuously injected at about 76 L/min (20 gpm) in Well TSF-05 to enhance the hydraulic gradient through the treatment cell. Based on previous tests, the effective porosity in the aquifer near Well TSF-05 was known to be extremely low (presumably due to years of use as a waste injection well), so rapid tracer breakthrough was anticipated at nearby monitoring wells. This required a high sampling frequency at Wells TAN-25 and TAN-31 in particular.

Tracer was injected for a period of about 30 minutes with an average bromide concentration of 12,000 mg/L. Figure 2 shows the tracer breakthrough curves at several monitoring points. The breakthrough at Wells TAN-25 and TAN-31 was very rapid as expected, with peak arrivals in less than 1 and 2 hours, respectively. A good breakthrough was also obtained at Well TAN-D2 (about 120 ft from the injection point) where the peak arrived in just under 4.5 days. The tracer arrival at Well TAN-37 was less well defined, with a lower, broader concentration peak, although it is only slightly further from the injection well than Well TAN-D2. In any case, it was verified that the tracer reached all of these observation points and arrival times were estimated. Tracer was not observed in TAN-26, presumably because it is completed about 30 m (100 ft) deeper in the aquifer (Figure 1) than Well TSF-05.

In addition to monitoring for tracer breakthrough, baseline sampling was performed at all of the wells on a weekly basis throughout the start-up period. Table 2 provides the average values measured for selected parameters. Well TAN-29 is not included because it is affected by dilution from the water reinjected in Well TAN-49. A blank in the table indicates the parameter was not measured. If a solute was not detected, a value of 0 is entered.

**TABLE 2. Average values measured for selected parameters before lactate injection.**

Well	DO (mg/L)	ORP (mV)	Nitrate (mg/L)	Sulfate (mg/L)	CO <sub>2</sub> (mg/L)	Lactate (mg/L)	Acetate (mg/L)	Propionate (mg/L)
TAN-10A	1.4	290	1.8	40	41	0	0	0
TAN-25			0.9	34	33	0	0	0
TAN-26	2.6	310	1.5	34	43	0	0	0
TAN-27	0.5	290	1.8	37	51	0	0	0
TAN-28	0.1	250	2.4	43	37	0	0	0
TAN-30A	0.1	260	2.6	41	48	0	0	0
TAN-31	0.5	250	1.0	36	38	0	0	0
TAN-37A	0.8	120	1.4	41	38	0	0	0
TAN-37B	2.0	180	1.9	39	45	0	0	0
TAN-D2	0.2	44	1.5	40		0	0	0

**Initial Lactate Injection Effects.** One round of ground water sampling was completed in January 1999 following the first two weekly lactate injections. Although a lag period was expected before significant microbial utilization of lactate occurred, significant changes were observed at monitoring wells near the injection well in less than 2 weeks. Table 3 gives the values of the parameters in Table 2 measured just 11 days after the first lactate injection.

**TABLE 3. Measured values for selected parameters 11 days after initial lactate injection.**

Well	DO (mg/L)	ORP (mV)	Nitrate (mg/L)	Sulfate (mg/L)	CO <sub>2</sub> (mg/L)	Lactate (mg/L)	Acetate (mg/L)	Propionate (mg/L)
TAN-25	0.0	-230	0.2	3	54	2600	42	61
TAN-26	0.0	-150	0.2	34	56	1500	23	31
TAN-28	0.0	250	2.3	39	35	0	0	0
TAN-30A	0.0	260	2.1	41	44	0	0	0
TAN-31	0.0	40	0.1	40	31	62	0	0
TAN-37A	0.2	-42	0.2	32	37	33	0	0
TAN-37B	0.1	-42	1.2	36	40	66	0	0
TAN-D2	0.3	-143	0.1	36	51	0	0	0

Comparison of Tables 2 and 3 reveals that lactate injection had a pronounced effect on several parameters of interest at all of the wells in Table 3 except the two furthest from the injection location, TAN-28 and TAN-30A. The conditions in the ground water have become more strongly reducing as reflected by decreases in dissolved oxygen (DO), oxidation reduction potential (ORP), nitrate, and even sulfate in TAN-25. The carbon dioxide concentrations increased in the two wells with the highest lactate concentrations, probably as a result of increased microbial activity. The presence of acetate and propionate is almost certainly associated with the biodegradation of lactate.

The in situ sonde deployed in Well TAN-37 has also provided some very interesting preliminary data. The sonde is located immediately above the pump associated with sampling location TAN-37A and measures a variety of parameters on a 4-hr interval. Figure 3 shows the ORP and specific conductivity measured in situ for the period of January 18 to January 25, 1999. An inverse correlation in which local maxima for ORP correspond to local minima for specific conductivity and vice versa is readily apparent. This correlation suggests that the combination of these two parameters serves as a surrogate for lactate.